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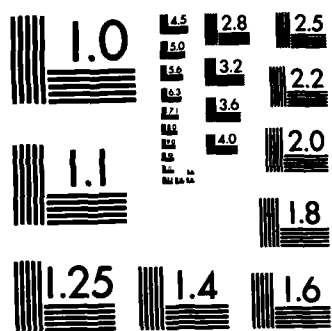
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Catalytic Reduction of Nitrogen Dioxide

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and

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Aerophysics Laboratory
Laboratory Operations
The Aerospace Corporation
El Segundo, Calif. 90245

30 September 1982

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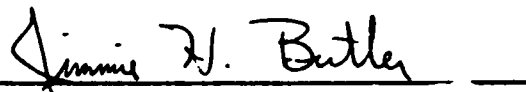
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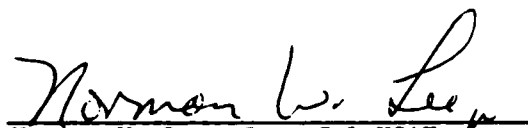


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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The feasibility of using a noble metal catalytic reactor to treat the effluents from a scrubber or incinerator treating N ₂ O ₄ /NO ₂ at space shuttle launch sites and other STS facilities has been explored experimentally in the laboratory. The major objective of the test program is to measure the efficiency of reduction of NO ₂ at concentrations of a few thousand parts per million in an inert gas diluent to threshold limit value levels. The catalytic reduction is accomplished with an admixture of CO to the NO ₂ diluent gas mixture. The optimum		

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ratio of CO and NO₂ for effective reduction in the reactor has been determined over a wide range of temperatures. The experiment was scaled down from field requirements because of laboratory constraints. However, the residence time of the reactants in the reactor was set at less than 40 msec to approximate presumed field conditions. The test results indicate very high (99.5%) overall efficiency for the removal of NO₂ from the diluent gas stream with the optimum admixture of the reducer gas. The maximum NO_x content of the effluent is shown to be less than 10 ppm under these optimal conditions.

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L. M. Hammond and S. B. Greeson assisted with preparation of the manuscript.

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CONTENTS

ACKNOWLEDGMENTS.....	1
I. INTRODUCTION.....	7
II. BACKGROUND.....	9
III. APPARATUS.....	11
IV. PROCEDURE.....	15
V. RESULTS AND DISCUSSION.....	17
A. Optimal Values for ϕ	17
B. Mass Balance Determination.....	23
C. Chemical Reactions Involved in the Catalytic Reduction of NO_2 to N_2 Using CO.....	25
VI. RECOMMENDATIONS.....	27
REFERENCES.....	29
APPENDIX: SCALE-UP CATALYTIC REACTOR TESTS FOR NO_2 UNDER FIELD CONDITIONS.....	31

FIGURES

1.	Modified Configuration of Catalytic Reactor.....	12
2.	Schematic of Experimental Arrangement in Fume Hood.....	13
3.	Variation of Concentrations of NO and CO in Effluent Gas Stream as a Function of Temperature and ϕ	22

TABLES

1.	Summary of All Tests of NO ₂ Reduction by CO on Pt-Rh Catalyst.....	18
2.	Dependence of Catalytic Reduction of NO ₂ on Residence Time of Gas Mixture in Reactor.....	21
3.	Mass Balance Verification by Gas Chromatography.....	24

I. INTRODUCTION

Methods for controlling the release of oxidizer ($\text{N}_2\text{O}_4/\text{NO}_2$) vapors below threshold limit values at space shuttle launch facilities and other STS facilities have been studied for some time. The excessive accidental release of the oxidizer can result from spillage at the site. Controlled release is required during propellant transfer, line purge, and tank depressurization.

Liquid scrubbers and flame incineration have been used as control measures when ($\text{N}_2\text{O}_4/\text{NO}_2$) concentration has been as high as several percent by volume in air or in an inert gas like N_2 . In the Space Shuttle Program, the effluent is ($\text{N}_2\text{O}_4/\text{NO}_2$) and could reach concentrations higher (50%) than that found in industrial applications. The threshold limit value of 5 ppm for NO_2 is difficult to achieve by either of these primary control techniques. A second-stage treatment of the tail gas from either of these primary devices using catalytic reduction of the residual NO_x was therefore proposed.

Although catalytic reduction has long been recognized as an effective control technique, the large pressure drop through dense beds of granular or pelletized catalysts had limited its development until the introduction of ceramic catalyst supports in the form of a lightweight, compact honeycomb structure.¹ Pressure drops across the honeycomb configuration are very low, and this configuration could provide more uniform gas flow and less chance for erosion of the active and support material.

The commercial availability of prefabricated, low cost units from the automobile industry and their capacity to treat large gas flows make this an attractive technique to explore. Typical catalytic converters on large automobiles or light trucks handle total gas flows comparable in volume to projected vent gas flows at the shuttle launch facilities. Also, the gas composition in this specific application is "clean" and easier to treat than automobile exhausts, because it is free of decomposition products from lubricating oil additives and trace quantities of anti-knock derivatives present in small quantities even in unleaded gasoline.

This laboratory test program was undertaken to assess the feasibility of using a standard automotive noble metal catalyst to reduce the NO_2 concentration from purge and transfer operations at shuttle launch facilities from a few thousand parts per million to environmentally acceptable levels. Carbon monoxide was chosen as the reducing gas instead of NH_3 (used in many industrial facilities). The acceptable operating range for the ratio of reducer gas (CO) to reactant (NO_2) for the efficient reduction of NO_2 to low NO_x with no residual CO had to be determined for a wide variety of operating parameters, such as NO_2 concentration in the flow, operating temperature of the reactor, residence time of gases in the system, and mole ratio of reactants. The potential for scale-up of the system from laboratory to field use was also examined.

II. BACKGROUND

The ratio, ϕ , of reducer gas (CO) concentration to reactant concentration (NO_2) is given by

$$\phi = \frac{\text{moles/min of CO}}{\text{moles/min of NO}_2}$$

A large number of bottles of NO_2/He and CO/He at various concentrations from 100 to 5000 ppm were purchased to make up the appropriate test mixtures. ϕ could be varied by changing the relative flow rates of the respective gas mixtures for every set of reduction tests.

III. APPARATUS

A principal component of the test system is a commercially made catalytic converter designed for a specific model automobile. The ratio of Rh to Pt on the surface of this unit is higher than all other commercial units. It was necessary to construct special flanges to use the catalytic reactor. Heating was provided with a resistively heated tubular furnace.

To achieve residence times of 100 ms or less, the gas flow was confined to the central portion of the honeycomb, as illustrated in Fig. 1. The 1/2-in. entrance and exit pipes were sealed onto the uneven honeycomb surface with a high-temperature, nonpoisoning gasket made of fiberfax. Cracks in the flows outside the 1/2-in. column were reduced to less than 1% of the total flow. The leakage flow was monitored continuously using a calibrated flowmeter.

Two preheaters, each consisting of approximately 21 ft of 1/4-in. stainless steel tubing, were mounted in tandem and enclosed by two separate tubular furnaces. The temperature was monitored at the entrance and exit points of the reactor using thermocouples. Flowmeters calibrated for He were used to measure input gas flow. A schematic of the apparatus is shown in Fig 2.

The analytical instruments used included an Energetic Science ECOLYZER/Model 7000 dual monitor for NO and NO₂ and an Energetic Science Model 2400A monitor for CO. The NO monitor has two ranges, 0 to 10 and 0 to 50 ppm, respectively. The NO₂ monitor has two ranges, 0 to 2 and 0 to 10 ppm, respectively. The CO monitor also has two ranges, 0 to 100 and 0 to 500 ppm, respectively. Further detailed analysis for N₂, CO₂ and O₂ was performed using two gas chromatographs. One system utilized a dual column consisting of a chromosorb 102 and molecular sieve 13X, which operated in series, with trapping of the CO₂ fraction in the chromosorb column to prevent entry into the sieve material. Another column used for analysis of N₂, O₂, and CO was a 22-ft silica gel column.

The basic chemical reactions that resulted in the catalytic reduction of NO₂ are discussed in Section V.

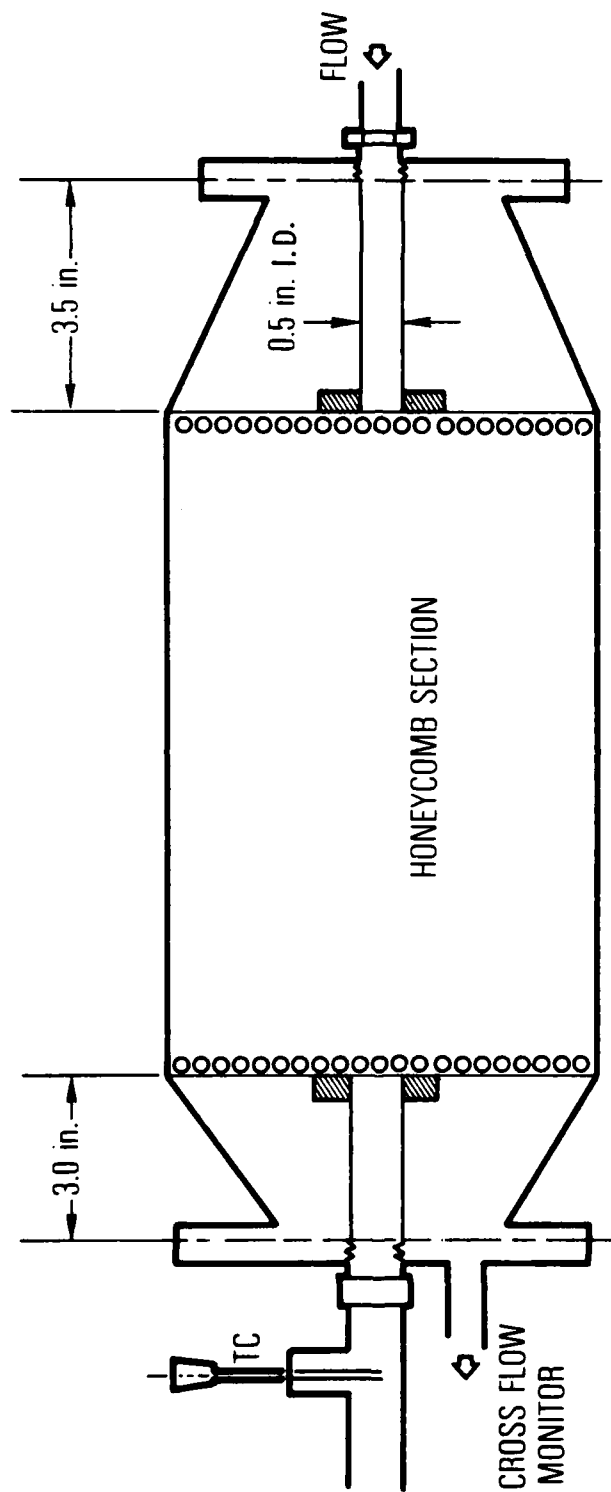


Fig. 1. Modified Configuration of Catalytic Reactor

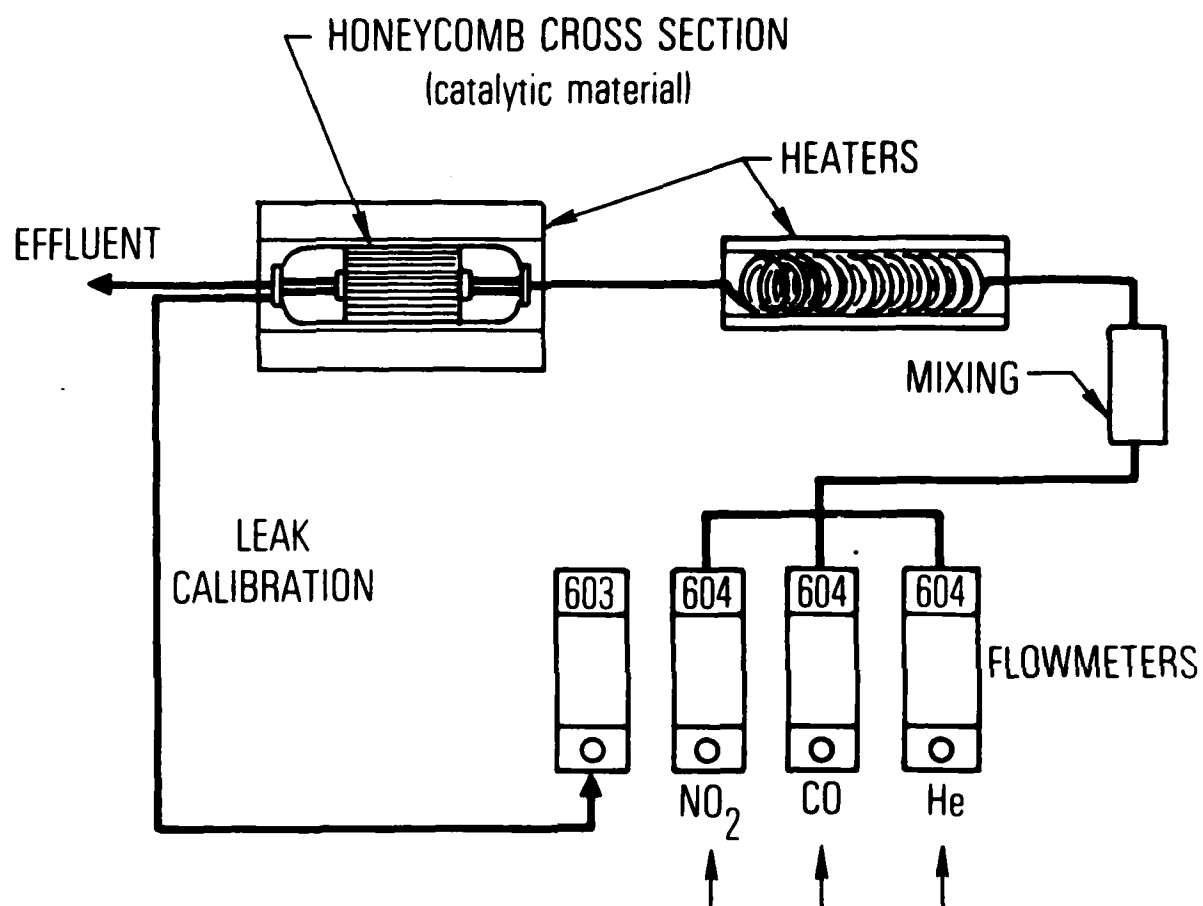


Fig. 2. Schematic of Experimental Arrangement in Fume Hood

The entire system was set up under a laboratory fume hood. Premixed and certified mixtures of He and NO_2 or CO at concentrations of 500, 2000, and 5000 ppm were used. The NO_2 concentration in the premixed gases showed a maximum variation of $\pm 4\%$ from the ordered values.

IV. PROCEDURE

All the tests were conducted in a laboratory fume hood. The analytical instruments were also kept under the hood. The highest concentration of CO and NO₂ used in these experiments was 5000 ppm for both gases in He.

The catalytic reactor furnace and the preheaters were turned on, and temperatures were measured at a position between the furnaces and at the exit of the reactor using He as the test gas. Measurements were made continuously until the reactor reached constant temperature, and isothermal conditions were achieved for the gas flow into and out of the reactor. At high gas flow rates and high temperatures, the temperature of the gas flowing into the converter could be maintained within 40°C of the reactor temperature. Pressures of approximately 8 psig were required to maintain the flows through the reactor. Gas flows were set for

1. A precalculated total flow to establish residence time.
2. A ratio of flows NO₂-He and CO-He to establish ϕ values for a given temperature.

The cross flow (if any) was constantly monitored using a separate flowmeter at the exit of the peripheral volume.

The temperature range covered in these experiments was from 300 to 475°C for the reactor. At each temperature setting, the effluent gas was sampled using a grab bag and analyzed for CO, NO, and NO₂ concentration. Samples were taken and analyzed every few minutes until steady-state output was reached. Under these conditions, the data gathered are identified in relation to a ϕ value, NO₂ concentration, temperature, and a residence time. Separate sets of experiments were conducted at two additional residence times to determine the effect of longer contract times upon reduction efficiency.

The Energetic Science monitors for NO, NO₂, and CO were calibrated using standard calibrating gas mixtures. Grab effluent gas samples were taken in 500 cc stainless steel test bottles under continuous flow conditions for gas chromatographic and mass spectrometric analysis to determine the CO₂, O₂, and H₂ content of this product gas.

V. RESULTS AND DISCUSSION

A series of tests was run under a wide range of operating parameters such as total gas flow rate, NO_2 concentration, reactor temperature, and ϕ value for the oxidizer to assess the performance characteristics of a noble metal catalytic reactor for the removal of residual NO_2 in an inert gas stream. The results of these tests are presented in Table 1. The effect of varying residence times upon reduction efficiencies is shown in Table 2. Lengthening the contact time from 33 to 132 msec does not appear to enhance reduction efficiency. Helium was chosen as the inert diluent gas for these tests instead of N_2 to facilitate unequivocal detection of reaction products. The overall system efficiency for removal of NO_2 from the gas streams at optimum admixture of the reducer gas CO has been found to be very high (~99.5%) at input concentrations of NO_2 of 2000 ppm and below. However, the reactor performance is found to be degraded at these temperatures when the gas stream contains oxygen as well.² This latter observation was made from test runs using one batch of bottled NO_2 in He from the supplier, in which the NO_2 was made up from NO with an excess of O_2 added to ensure complete oxidation. No O_2 is anticipated to be present in the vent gas during normal operations except when the aspirators are in use. The use of a burner would introduce considerable excess O_2 in order to maintain a flame. This must be alleviated by the capability to control both air and fuel flow. So far, no tests have been made with a burner-catalyst system. Such tests are required to establish feasibility.

A. OPTIMAL VALUES FOR ϕ

The NO and CO concentrations in the effluent gas stream as a function of ϕ for each reactor temperature are given in Figs. 3a and 3b. Air-pollution regulations require the concentrations of both NO_x and CO to be below 50 ppm. The catalyst can easily meet this requirement over a range of different values for ϕ . The range varies somewhat as the catalyst temperature is changed. There is a slight upward trend as the temperature is raised from 300 to 450°C. This is, however, reversed at 475°C.

Table 1. Summary of All Tests of NO₂ Reduction by
CO on Pt-Rh Catalyst^a

Temperature (°C)	φ	[NO ₂] (ppm)	[CO] (ppm)	Total Flow (l/min)	Residence Time (msec)	[NO] _{out} (ppm)	[CO] _{out} (ppm)	[NO ₂] _{out} (ppm)
300	1.5	800	1200	35	33	50	0	0.2
300	1.6	770	1230	35	33	6	0	0.1
300	1.66	752	1248	35	33	4	4	---
300	1.7	740	1260	35	33	4	13	0
300	1.8	715	1285	35	33	2.5	105	0
350	1.6	770	1230	35	33	>50	0	2
350	1.7	740	1260	35	33	18	0	1
350	1.76	725	1275	35	33	6	6	---
350	1.8	715	1285	35	33	1.8	20	0
350	1.9	690	1310	35	33	0.2	110	0
400	1.7	740	1260	35	33	>50	0	5
400	1.8	715	1285	35	33	14	0	0.8
400	1.83	704	1296	35	33	9	9	---
400	1.9	690	1310	35	33	1.0	75	0
450	1.7	740	1260	35	33	>50	0	4
450	1.8	715	1285	35	33	38	0	0.75
450	1.86	700	1300	35	33	11	11	---
450	1.9	690	1310	35	33	2.5	37	0
450	2.0	667	1333	35	33	0	110	0
475	1.5	2000	3000	35	33	17	0	0
475	1.7	1852	3148	35	33	0.6	20	0
475	1.8	1786	3215	35	33	8	0	1

^aTest data for concentrations of NO₂ in He varying from 160 to 2000 ppm

Table 1. Summary of All Tests of NO₂ Reduction by CO on Pt-Rh Catalyst (Continued)

Reactor	Input Concentration				Effluent Concentration				
Temperature (°C)	φ	[NO ₂] (ppm)	[CO] (ppm)	Total Flow (l/min)	Residence Time (msec)	[NO] _{out} (ppm)	[CO] _{out} (ppm)	[NO ₂] _{out} (ppm)	
300	1.6	192	308	35	33	>50	0	1.2	
300	1.7	185	315	35	33	18	0	0.8	
300	1.8	179	321	35	33	5.5	0	0.6	
300 → ^b	1.9	172	328	35	33	1.1	0	0	
300	1.91	172	328	35	33	1.0	1.0	---	
300	2.0	167	333	35	33	0.8	17	0	
300	2.1	161	339	35	33	0.3	47	0	
350	1.5	200	300	35	33	>50	0	1.0	
350	1.6	192	308	35	33	47	0	0.6	
350	1.7	185	315	35	33	19	0	0.4	
350	1.75	182	318	35	33	5	0	0.2	
350 →	1.8	179	321	35	33	1.5	0	0.1	
350	1.91	172	328	35	33	1	1	---	
350	1.9	172	328	35	33	0.2	8	0	
350	2.0	167	333	35	33	0.2	30	0	
350	2.1	161	339	35	33	0 ⁺	52	0	
350	2.25	154	346	35	33	0.2	80	0	
400	1.6	192	308	35	33	>50	0	1.5	
400	1.7	185	315	35	33	20	0	0.5	
400 →	1.8	179	321	35	33	2	0	0	
400	1.81	178	322	35	33	2	2	---	
400	1.9	172	328	35	33	0.5	27	0	
400	2.0	167	333	35	33	0.5	37	0	
450	1.7	185	315	35	33	30	0	0.6	
450	1.8	179	321	35	33	6.5	0	0.2	
450	1.9	172	328	35	33	3.5	0	0	
450	1.94	170	330	35	33	3.0	3.0	---	
450 →	2.0	167	333	35	33	2.5	13	0	

^bThe arrows indicate the optimum values for φ.

Table 1. Summary of All Tests of NO₂ Reduction by
CO on Pt-Rh Catalyst (Continued)

Reactor Temperature (°C)	φ	Input Concentration		Residence Time (msec)	Effluent Concentration			
		[NO ₂] (ppm)	Total Flow [CO] (l/min)		[NO] _{out} (ppm)	[CO] _{out} (ppm)	[NO ₂] _{out} (ppm)	
300	1.5	2000	3000	35	33	>50	0	0.4
	1.55	1960	3040	35	33	8.8	0	0.25
	→ 1.6	1920	3080	35	33	1	0	0
	1.60	1920	3080	35	33	1	1	---
	1.7	1850	3150	35	33	0.3	67	0
325	1.8	1785	3215	35	33	0 ⁺	330	0
	1.5	2000	3000	35	33	750	0	3
	1.55	1960	3040	35	33	38	0	2
	→ 1.6	1920	3080	35	33	5	0	1
	1.61	1915	3085	35	33	3	3	---
375	1.75	1820	3180	35	33	0.5	300	0
	2.0	1670	1330	35	33	1	>500	0
	1.6	1920	3080	35	33	>50	0	5
	→ 1.7	1850	3150	35	33	3	0	0.3
	1.7	1850	3150	35	33	3	3	---
425	1.75	1820	3080	35	33	2	130	0
	1.8	1785	3215	35	33	0	370	0
	1.7	1850	3150	35	33	>50	0	7.5
	1.75	1820	3180	35	33	>50	0	3.5
	→ 1.8	1785	3215	35	33	5	0	0.4
	1.81	1780	3220	35	33	4	4	---
	1.85	1755	3245	35	33	1.5	33	0
	1.9	1725	3275	35	33	0 ⁺	300	0
	2.0	1670	1330	35	33	0	330	0

Table 2. Dependence of Catalytic Reduction of NO₂ on Residence Time of Gas Mixture in Reactor

τ/msec	Temp (°C)	ϕ	[NO ₂]	[NO]	[CO]	[NO ₂] input
33	300	1.66	0	4	13	750
33	350	1.74	0	1.8	20	750
33	400	1.83	0	1	0	750
33	450	1.85	0	0.5	37	750
66	300	1.5	0	3.5	4	750
66	350	1.5	0	3	40	750
66	400	1.55	0	4	33	750
66	450	1.64	0	3	40	750
132	300	1.57	0.4	4.5	13	750
132	350	1.64	0.6	2.6	28	750
132	400	1.73	0.5	0	7	750
132	450	1.66	0	6	28	750

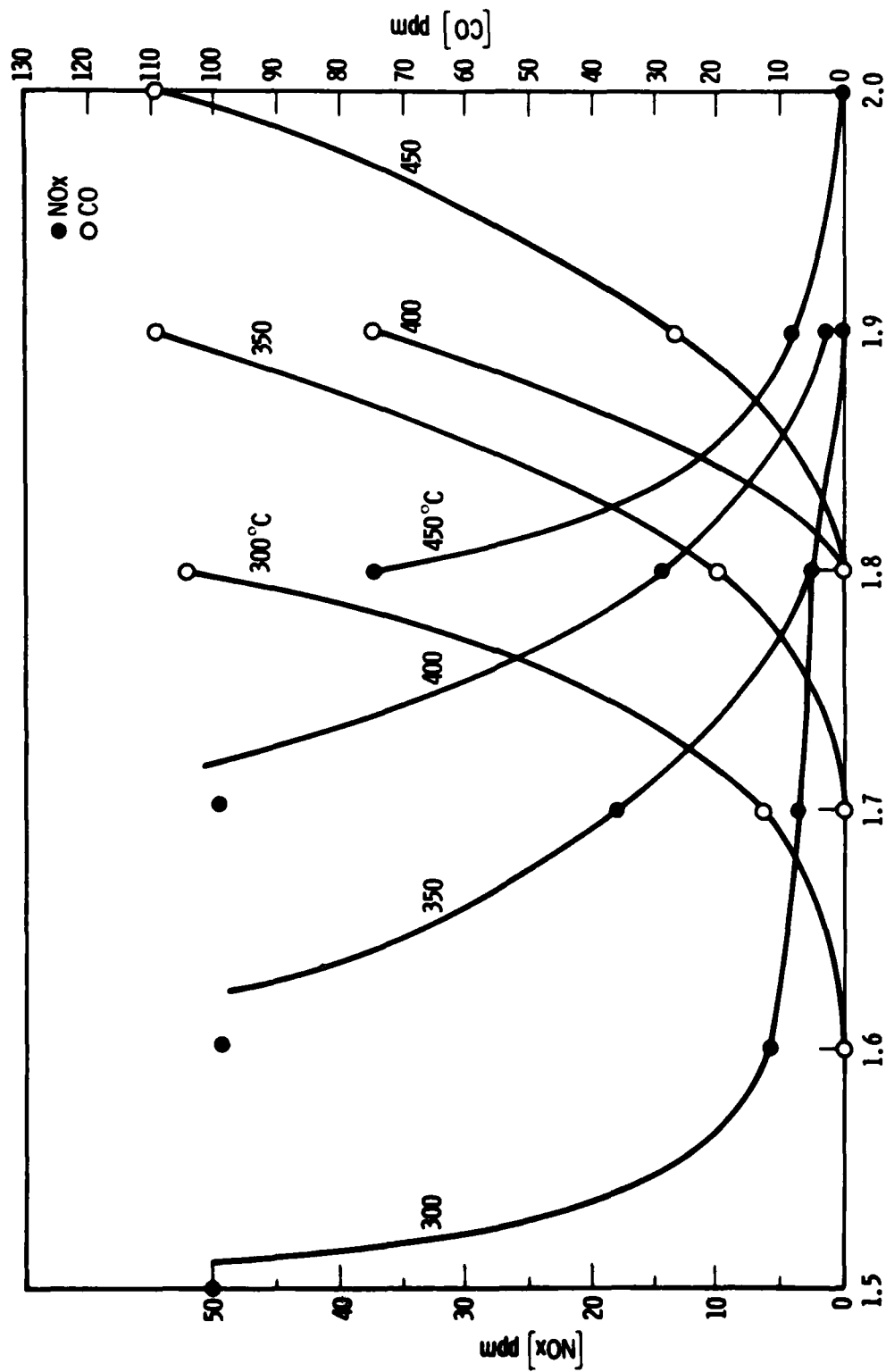


Fig. 3. Variation of Concentrations of NO and CO in Effluent Gas Stream as a Function of Temperature and ϕ

<u>Catalyst Temperature</u>	<u>Values of ϕ for which</u>
<u>(°C)</u>	<u>both NO_x and CO are > 50 ppm</u>
300	1.50 to 1.78
350	1.64 to 1.85
400	1.75 to 1.88
430	1.70 to 2.00
450	1.80 to 1.95
475	1.50 to 1.80

B. MASS BALANCE DETERMINATION

Under optimum conditions of operation, the only reactor products are N₂ and CO₂. Trace amounts of O₂ have also been detected. However, O₂ tends to get absorbed as O atoms on Pt surfaces and can be effectively desorbed only at a higher temperature than the range covered here. This does not produce irreversible poisoning of the catalyst.³ At temperatures above 500°C the observed performance degradation as a result of entrained oxygen may be insignificant.

The sensitivity of the gas chromatographic technique to estimate effluent concentration is not good enough for concentrations below 100 ppm. Trace constituents in this efflux cannot therefore be quantitatively estimated by this instrument. Typical gas chromatographic analysis data are presented in Table 3. The last two columns provide the concentrations of product N₂ and CO₂ in parts per million in the effluent gas stream.

When the reactions proceed to completion at optimum value of ϕ as discussed earlier, the CO₂ output concentration ideally should equal the CO input concentration. Also, the N₂ content of the efflux in the ideal case should be one-half that of the NO₂ input.

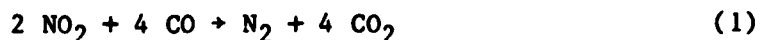
Results of the three mass balance determinations showed that the CO₂ concentrations varied from +3 to -20% from the expected amount based on the input of CO. Likewise, the N₂ concentration varied from +7 to +13% of the expected amount. The catalytic reduction process for NO₂ appears to be complete.

Table 3. Mass Balance Verification by Gas Chromatography

Run No.	Ratio ϕ	Input conc. NO ₂ (ppm)	Input conc. CO (ppm)	Effluent conc. NO ₂ (ppm)	Effluent conc. CO (ppm)	Effluent NO conc. (ppm)	Reactor Temperature (°C)	Output conc. N ₂ (ppm)	Output conc. CO ₂ (ppm)
001	1.6	808	1292	0.1	0	6	300	440	1030
006	1.7	777	1322	0.0	35	1	450	440	1360
007	1.8	750	1350	0.0	20	0.4	450	400	1090

C. CHEMICAL REACTIONS INVOLVED IN THE CATALYTIC
REDUCTION OF NO₂ TO N₂ USING CO

A reaction that leads to complete reduction of NO₂ is



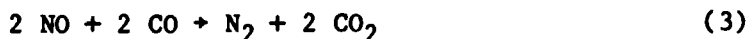
If this is the major reaction path, an optimum value of $\phi = 2$ will prevail. However, the experimental data indicate generally, that the ϕ_{opt} is less than 2 and is also a weakly dependent function of reactor temperature. The observed increase in the concentration of NO in the effluent gas stream as the CO flow is reduced below its optimum value (Fig. 3) leads us to believe that other reactions also should be considered.

The decomposition reaction



is considered to be a competing reaction.

The product NO is subsequently reduced in the reaction



The equilibrium constants⁴ at 700 and 573 K have been calculated for reaction (2). Conversion efficiencies of 97 and 78%, respectively, are found at these temperatures. Gas chromatographic analysis of the effluent in this CO lean mode of operation shows the presence of O₂ giving qualitative support to this reaction sequence. The higher probability of a two-step reaction as indicated earlier has also been found in work performed at the General Motors Research Laboratories.⁵

The dissociation of the product CO₂ to form CO and O₂ in the catalytic reactor is highly unlikely.

VI. RECOMMENDATIONS

On the basis of the results of this investigation on the reduction of NO_2 at concentrations of about 2000 ppm or less in He, the following recommendations were made:

1. A similar study should be undertaken of scaled up flows up to 100 ft^3/min at the same NO_2 concentrations as in the current tests. Since the gas flow in the present tests is restricted to only about 1% of the reactor volume, the same unit can be used to test the reduction efficiency of NO_2 at 100 times the present flow rate, and the same residence time. Total flows in excess of 100 ft^3/min would be required. The reactor, furnace, and enlarged or modified preheaters used in these tests can be used for the scaled up experiment. Some scale-up estimates to accomplish this task are given in the Appendix.
2. The laboratory measurements should be repeated with NO_2 concentrations of up to 5000 ppm in He.
3. The effect of other reducing agents such as propane and natural gas on NO_2 control in the catalytic reactor should be investigated.
4. The effect of oxygen, soot, and low concentrations of reducing gas upon overall catalytic efficiency should be studied.
5. The use of H_2 as the fuel offers several advantages. Fuel rich H_2 -air flames do not soot or generate CO. Also, under excess H_2 burning conditions the production of flame produced NO_x is minimized. No restrictions are presently enacted preventing the emission of small quantities of H_2 . The use of H_2 in a catalytic afterburner is a standard procedure in industry,¹ if it is necessary to use such a device to reach allowable NO_x emission levels.
6. Close liaison should be maintained with working groups at General Motors and Ford Research Laboratories and catalyst reactor manufacturers such as Johnson-Mathey and Englehardt Industries for newer technological developments in this field.

REFERENCES

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APPENDIX

SCALE-UP OF CATALYTIC REACTOR TESTS FOR NO₂ UNDER FIELD CONDITIONS

Modifications required to handle 100 scfm of total gas flow to simulate field conditions are discussed herein. It has been suggested that N₂, instead of He, be used as the diluent gas for these tests on the basis of cost and the substantially lower heat capacity of N₂ compared with He.

The gas handling system must handle 40 scfm of nitrogen containing 2000 ppm NO₂ and 60 scfm of nitrogen containing 2000 ppm CO. The gases will be premixed in standard gas cylinders containing 200 scf at an initial pressure of 2000 psi.

The equipment required is readily available. Matheson Model 9, two-stage regulators will pass 50 scfm at an inlet pressure of 200 psi. This will handle the projected flow of NO₂ in N₂. Flow of CO in N₂ can be sustained using two bottles with regulators in parallel. One bottle of NO₂ will run for 4 to 5 min at constant flow of 40 scfm. Flowmeters to handle 100 scfm of N₂ at 200 psi are in current use in the Aerophysics Laboratory. Half-inch diameter stainless steel tubing and fittings can handle these flows at 200 psi.

A pressure of 200 psi in 1/2-in. tubing will be reduced to near-atmospheric pressure after entering the catalytic reactor. The area of cross section of flow is increased by a factor of 100 when the collimating adapter is removed.

The total flow of 100 scfm of N₂ with NO₂ and CO must be heated from 20 to 350°C before entering the reactor to avoid any cooling of the reactor that might affect its performance. This requires the addition of 3 kW of heat to the gas stream; it is not as difficult as heating helium, which has five times the heat capacity of N₂. The following methods of heating the gas are being considered. A bed of hot ceramic beads might provide the best heat transfer for transient runs of 5-min duration. A continuous-duty heat exchanger system is also a possibility and could be either electrically driven or run with a

burner. Electrical-resistance heating of large gas flows is also being performed in the Aerophysics Laboratory, and a device using this technique is available for use.

Disposal of 100 scfm of N_2 , with traces of unreacted NO_x and CO, must be addressed. The laboratory fume hood is rated at 150 linear ft/min with an area of 10 sq ft. This means a total flow of 1500 scfm. Our effluent flow of 100 scfm therefore will be diluted by a factor of 15. Since the reactor has already been proven to reduce NO_x levels well below 50 ppm, we expect to reach threshold limit value levels of 5 ppm even before dilution.

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